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(54) **Bleach compositions.**

(57) A bleach composition comprises an active halogen or a peroxy bleach material, preferably hypochlorite; surfactant; and polymeric thickener comprising charged, hydrophilic monomer and uncharged hydrophobic monomer. The polymeric thickener preferably comprises a copolymer of methacrylic acid and styrene having proportions (wt%) of methacrylic acid and styrene ranging from 80:20 to 20:80, and preferably comprises 54 wt% methacrylic acid and 46% styrene, with a molecular weight of about 100,000 and substantially no cross-linking. The polymeric thickener acts to enhance thickening and enables use of a wider range of surfactants than hitherto possible.

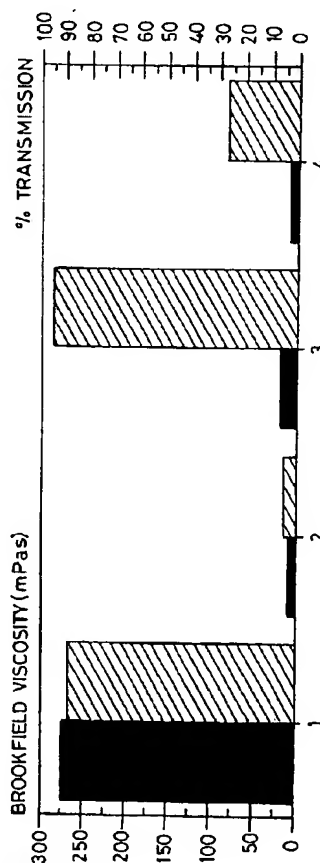


Fig. 1

Field of the invention

This invention concerns bleach compositions, particularly thickened aqueous bleach compositions.

5 Background to the Invention

There is much prior art concerning thickened aqueous bleach compositions, using a variety of thickening agents. See, for example, EP 0256638 (Clorox), EP 0373864 (Procter & Gamble) and EP 0329419 (Unilever) and the prior art referred to in those documents.

10 Summary of the Invention

According to the present invention there is provided a bleach composition, comprising an active halogen or a peroxy bleach material; surfactant; and polymeric thickener comprising charged, hydrophilic monomer and uncharged, hydrophobic monomer.

The charged, hydrophilic monomer is preferably selected from the group: acrylic acid and substituted acrylic acids, eg. methacrylic acid, maleic acid and half-esters thereof, crotonic and itaconic acids and other alkene carboxylic acids and their derivatives, carboxylated styrene, sulphonated styrene, ethylene sulphonic acid, and certain nitrogen-based monomers eg acrylamide, vinyl pyrrolidone, and mixtures of such hydrophilic monomers.

The uncharged hydrophobic monomer is preferably selected from the group: styrene and substituted styrenes eg. alpha-methyl styrene, alpha-olefins, eg. C₁₂-alpha-olefin, vinyl ethers, eg. butyl vinyl ether; allyl ethers, eg. butyl allyl ether; unsaturated hydrocarbons, eg ethylene, propylene, cyclohexene and dienes, eg. 1,6 hexadiene, divinyl benzene, cyclohexadiene. Such hydrophobic moieties may also be introduced into the polymer by chain transfer agents and initiators; eg. mercaptans, eg. dodecyl mercaptans, and peroxides and azo initiators, eg. dilauryl peroxide, AZBN (azobis butyronitrile). Mixtures of hydrophobic monomers may also be used.

A single monomer with both hydrophilic and hydrophobic properties may also be used.

The preferred polymer comprises a copolymer of methacrylic acid and styrene, conveniently having proportions (wt %) of methacrylic acid and styrene ranging from 80:20 to 20:80.

Additional monomers, such as acrylic esters, acrylates, olefins and substituted styrenes, may optionally be included, eg in place of up to about half of the amount of styrene.

The polymer is preferably substantially non cross-linked, for reasons that will be explained below, although a degree of cross-linking can be tolerated.

The polymer preferably has a molecular weight of about 100,000, although this is not critical and indeed it can be difficult to produce a polymer having an accurately specified molecular weight. Molecular weights in the range 80,000 to 120,000 are thus regarded as about 100,000. If the molecular weight is substantially lower, then this has a deleterious effect on thickening properties of the polymer. Further, if the molecular weight of the polymer is too high, then clarity and stability of the composition can be adversely affected.

One particularly preferred polymer comprises 54 wt% methacrylic acid and 46% styrene, with a molecular weight of about 100,000 and substantially no cross-linking. Such a polymer is found to be hypochlorite-stable and to be an effective thickener in hypochlorite bleach.

Such polymers can be readily made in conventional manner, eg by emulsion polymerisation.

The polymer is present in an appropriate amount to achieve thickening to a desired degree, and is typically present in an amount from 0.1 to 7.5% by wt as active material, preferably 0.5 to 3% by wt as active material. Suitable amounts for any particular composition can be readily determined by experiment, depending on bleach concentration, target viscosity and other considerations. In general, the greater the concentration of bleach material, the greater the amount of polymer (and also surfactant) required to achieve a given viscosity.

The bleach material may comprise one or more peroxy compounds, as are well known in the art, including peracids and salts thereof, and hydrogen peroxide and derivatives thereof. Preferably, however, the bleach material comprises one or more halogen compounds, as are also well known in the art, including alkali metal and alkaline earth salts of hypochlorite, haloamines, haloimines, haloimides and haloamides. Hypochlorite and compounds producing hypochlorite in aqueous solution are preferred. Particularly preferred is sodium hypochlorite, NaOCl, typically in an amount ranging from 0.2 to 15% by weight, more preferably 0.2 to 10% by weight, and typically providing an amount of available of chlorine in the range 1 to 5% by wt.

The surfactant has a cleaning function, and it is possible to use a single surfactant or a mixture of surfactants selected from a wide range, including the following: alkyl ether sulphates, eg. lauryl ether sulphate, such as those sold under the Trade Names Empicol ESB3 (Na salt with 2 ethylene oxide (EO) units), Empicol MD,

(Na salt, 4EO), Empimin KSN and Perlankrol ESD (both Na salt, 3 EO), alcohol sulphates, eg lauryl alcohol sulphate, such as those sold under the Trade Names Empicol LZV and Empicol LX28, tallow alcohol sulphates, such as those sold under the Trade Name Empicol TAS30, alkyl benzene sulphonates, eg that sold under the Trade Name Nansa SL30, paraffin sulphonates, eg that sold under the Trade Name Lutensit A-PS, alkyl phenol ether sulphates, eg. those sold under the Trade Names Perlankrol PA conc, Perlankrol SN, and Perlankrol RN75, alcohol ethoxylates, eg. those sold under the Trade Names Dobanol 91-6, Ethylan CD 91-6, Empilan KC8 and Synperonic A7, nonylphenol ethoxylates, eg that sold under the Trade Name Ethylan BCP, sodium carboxylates (soaps) (salts of fatty acids) manufactured from fatty acids such as those sold under the Trade Names Prifac 7908, and Prifac 6920, by neutralisation of the acid with a base eg sodium hydroxide or triethanolamine; alkyl ether carboxylates, eg that sold under the Trade name eg. Olin CS1, alkyl polyglucosides, eg. those sold under the Trade Name Plantaren, EP/PO block copolymers, eg those sold under the Trade Plurafac, Triton, and Monolan PC, alkyl diphenyloxide sulphonates eg. that sold under the Trade Name Dowfax 3B2, fatty acid amides, eg those sold under the Trade Names Empilan CME/CDE, acyl sarcosinates, alkyl taurides, sulphosuccinates, eg that sold under the Trade Name Empimin OT, alpha-olefin sulphonates, phosphate esters (alkyl and/or aryl), eg those sold under the Trade Name Phospholan, ethoxylated fatty acids, triethanolamine lauryl sulphate, eg that sold under the Trade Name Empicol TL40, triethanolamine alkyl benzene sulphonate, eg that sold under the Trade Name Nansa TS50, sodium alpha olefin sulphonate, eg that sold under the Trade Name Nansa LSS38.

Suitable mixtures of surfactants are generally found to give good results.

The composition is preferably substantially free of nonionic surfactant and nitrogen-based surfactant.

Good results have been obtained with lauryl ether sulphates, eg those sold under the Trade Names Empicol ESB3 (lauryl ether sulphate, Na salt, with 2 ethylene oxide units (2EO)), and Empicol MD (lauryl ether sulphate, Na salt, with 4 EO). A mixture of these two surfactants, eg in wt proportions of active matter of MD: ESB3 of 2:1, is found to give particularly good results in a hypochlorite bleach composition.

Surfactant is conveniently present in an amount in the range 0.5 to 5% by wt active matter, typically about 2% to 3% by wt active matter.

It is found that with compositions in accordance with the invention, including polymeric thickener, thickening of hypochlorite bleach can be obtained with less surfactant (typically 2-3% by wt active matter) than is possible in the absence of polymer. It is thought the polymer acts as a hydrotrope, and thickening arises due to the interaction of the polymer with surfactant rod micelles and not solely from the swelling of the polymer. As a result of these interactions, marked increases in viscosity can be obtained. Compositions in accordance with the invention can thus be more cost-effective than conventional compositions.

For a high bleach composition, (typically containing about 3-6% by wt active hypochlorite), such as a toilet or drain cleaner, it is found appropriate to use one or more relatively soluble surfactants (i.e. a surfactant for which a 10% solution in water has a cloud point below about 0°C, preferably below -3°C). If a surfactant of lower solubility is used, the surfactant will generally salt out and so not be appropriate.

Suitable relatively soluble surfactants include sodium lauryl ether sulphate (SLES) eg Empimin KSN or Perlankrol ESD, triethanolamine lauryl sulphate, eg Empicol TL40, and triethanolamine alkyl benzene sulphonate, e.g. Nansa TS50.

For a low bleach composition (typically containing up to 3% by wt active hypochlorite), such as hard surface and multisurface cleaners, it is found appropriate to use a mixture of relatively soluble surfactant (as defined above) and relatively insoluble surfactant (i.e. a surfactant for which a 10% solution in water has a cloud point above 0°C). Such relatively insoluble surfactants do not have a tendency to form hexagonal liquid crystal structures: instead these surfactants form lamellar liquid crystal structures at higher concentrations in water or hydrated crystalline structures.

Suitable relatively insoluble surfactants include sodium alkylbenzene sulphonate (LABS), e.g. Nansa SL30, sodium lauryl sulphate, e.g. Empicol LX28 and sodium alpha olefin sulphonate, e.g. Nansa LSS38.

The viscosity of such low bleach compositions can be controlled by varying the proportions and/or amount of relatively soluble surfactant and relatively insoluble surfactant.

Bleach products containing less than 3.0% active sodium hypochlorite have hitherto been particularly difficult to thicken with surfactants and mixtures of surfactants. This is due to insufficient electrolyte being present to bring about the necessary reductions in surfactant solubility. As surfactant solubility decreases rod micelles form and through tangling increase the solution viscosity. Increases in electrolyte level through additions of sodium chloride merely catalyze the decomposition of the sodium hypochlorite, and hence cannot be made. The present invention can thus overcome such difficulties.

For both high and low bleach compositions good thickening can be obtained with 2-3% by wt active matter surfactant and about 1/2% by wt active matter polymer.

The cleaning properties of such compositions have been tested and found to be good.

The polymer thus acts to enhance thickening and enables use of surfactants (and mixtures thereof) not previously possible. A wider range of surfactants is thus available for use in compositions in accordance with the invention so surfactants can be selected for cleaning properties and cost effectiveness.

The composition may optionally include electrolyte. Low levels of electrolytes such as sodium chloride function to provide ions in aqueous solution and have been shown to improve solution viscosity. Sodium chloride is generally present in sodium hypochlorite as available commercially, or may be added to the composition in appropriate amounts such that the stability of the sodium hypochlorite will not be adversely affected.

The composition may also optionally include buffer, to maintain pH. Alkaline pHs, typically between 11 and 14, eg about 13, are generally appropriate to achieve desired viscosity and stability. Some reagents function both as electrolyte and buffer.

Further optional ingredients such as fragrance, colouring agents, whiteners, solvents and builders may be included for aesthetic reason or to improve properties.

Particularly preferred compositions in accordance with the invention comprise hypochlorite bleach, the preferred methacrylic acid/styrene polymer discussed above (having 54% methacrylic acid and 46% styrene, a molecular weight of about 100,000 and being substantially non-cross linked), and surfactant. Where the amount of hypochlorite is greater than about 3% by wt active, the surfactant comprises sodium lauryl ether sulphate (SLES). Where the amount of hypochlorite is less than about 3% by wt active, the surfactant comprises a mixture of sodium alkylbenzene sulphonate (LABS) and sodium lauryl ether sulphate (SLES). These compositions are viscous, stable, isotropic formulations, with good cleaning and bleaching properties and good stability.

As mentioned above, it is preferred to use substantially non cross-linked polymer. Non cross-linked polymers are found to give compositions with better clarity than those using cross-linked polymer, particularly if perfume (which is generally an oil) is present in the composition.

Furthermore, a synergistic effect has been observed between surfactant and polymer that is also thought to be related to the state of cross-linking of the polymer: hypochlorite bleach containing both polymer and surfactant is found to have substantially improved characteristics of viscosity and clarity as compared with hypochlorite containing only polymer or only surfactant. This effect is not fully understood, but is much more marked with substantially non cross-linked polymer, and it is thought that the polymer interacts with the surfactant micelles in some way, as discussed above.

Compositions in accordance with the invention, in preferred embodiments at least, have certain advantages over similar prior art compositions, including the following:

1. They are substantially free of nitrosamines commonly associated with compositions using nitrogen-based surfactants such as amine oxides.
2. A wider range of surfactants can be used than has hitherto been possible, enabling surfactants to be selected for their cleaning properties and cost effectiveness.

The compositions of the invention find particular, but not exclusive, application in hard surface cleaning, eg of bathroom and kitchen surfaces.

The invention will be further described, by way of illustration, in the following examples and by reference to the accompanying drawings, in which:

- Figure 1 is a series graphs of viscosity and % transmission for various mixtures, with results for viscosity shown by solid bars and those for % transmission shown by hatched bars;
- Figure 2 is a further series of graphs similar to Figure 1;
- Figure 3 is a further series of graphs similar to Figure 1;
- Figure 4 is a graph of viscosity of various compositions in accordance with the invention, with various different amounts of mixtures of surfactant; and
- Figure 5 is a graph of viscosity over time for various compositions in accordance with the invention.

Example 1 Manufacture of Methacrylic Acid/Styrene Polymer

A substantially non-cross linked polymer (referred to as Polymer A) of methacrylic acid (54% wt) and styrene (46% wt) with a molecular weight of about 100,000 (characterised by GPC compared with polyacrylate standards) was made on a pilot scale by conventional emulsion polymerisation techniques. The materials used were as follows:

	<u>Grms</u>	<u>Remarks</u>
5	<u>Reactor charge</u>	
	Deionized water	4500
	Crodafos N3A	112.5
	.910 Ammonia soln.	37.5
10	Empilan KB3	180
	<u>Initial monomer</u>	
15	Methacrylic acid	210
	Styrene	150
20		Add at 70°C hold a further 15 mins. once the reactor temperature reaches 80°C.
	<u>Initial catalyst</u>	
25	Potassium persulphate	3
	Deionized water	280
		Add at 70°C with init. mons.
30	<u>Monomer (slow-add)</u>	
	Deionized water	3750
		Add over 3 hours at
35	Crodafos N3A	112.5
	Empilan KB3	180
	Methacrylic acid	2250
	Styrene	1935
40		80°C.
	<u>Catalyst (slow-add)</u>	
	Potassium persulphate	4.5
	Deionized water	1200
45		Add over 3½ hours
	<u>Scavenge</u>	
	Potassium persulphate	3
50	Deionized water	900
		Add over 1 hour

The procedure used was as follows.

55 The initial charge of deionised water and surfactants were added to a 15 litre stainless steel reactor fitted with a lid which has inlet ports for an agitator, water condenser and for the addition of monomer and initiator solutions. The contents of the reactor were heated to 80°C under nitrogen.

At 70°C a portion of the monomer and initiator solution were added to the reactor and were allowed to ini-

After initiation had taken place the monomer and the initiator solutions were added to the reactor concurrently over 3 hours and 3.5 hours respectively at 80°C. At the end of the initiator addition the reactor temperature was maintained at 80°C for a further 1 hour to eliminate any unreacted monomer. After completion of the 1 hour hold the emulsion polymer was cooled to less than 30°C, filtered and transferred to storage.

The resulting product was an aqueous dispersion of methacrylic acid/styrene copolymer, with the following typical properties.

Solids	= 31.75%
pH	= 2.6
Brookfield Viscosity (2/20rpm)	= 30mPas

Example 2. Behaviour of Polymer A in 5% Sodium Hypochlorite

In order to test the behaviour of polymer A in 5% sodium hypochlorite, various mixtures were made up as follows (all % are w/w active matter):

1.	Empicol MD	2%
	Empicol ESB3	1%
	Polymer A	1.74%
	NaOCl	5%

2.	Empicol MD	2%
	Empicol ESB3	1%
	NaOCl	5%

This mixture was non-homogeneous and separated overnight.

3.	Polymer A	1.74%
	Deionised water	balance to 100%

4.	Polymer A	1.74%
	NaOCl	5%

In all cases the pH was adjusted to 13 with NaOH.

For each mixture the % transmission at 500nm was tested to give an indication of clarity, and the viscosity at 3/20 rpm was also tested. The results are shown graphically in Figure 1, with solid bars indicating viscosity and hatched bars % transmission.

In Figure 1, bars 1 indicate results for mixture 1 above, bars 2 results for mixture 2, bars 3 results for mixture 3 and bars 4 results for mixture 4.

It can be seen from Figure 1 that polymer or surfactant alone in hypochlorite (mixtures 4 and 2, respectively) give poor results in terms of both clarity and viscosity. However, mixtures of polymer, surfactant and hypochlorite (mixture 1) give very good results in terms of both clarity and viscosity. A synergistic effect is thus occurring between the polymer and surfactant.

Example 3. Effects of cross-linked polymers on viscosity and clarity in unperfumed hypochlorite

In order to test the effects of cross-linked polymers on viscosity and clarity in unperfumed hypochlorite, a crosslinked version of polymer A (known as polymer B) was prepared by a similar process to that used to prepare polymer A.

Various mixtures of this polymer B (1.74% by wt active), surfactant (3% by wt active Empicol ESB3) and sodium hypochlorite (1.6% by wt active) were made up, with pH adjusted to 13 with NaOH. The viscosity at 20 rpm and % transmission at 450 nm were tested, and the results are shown graphically in Figure 2.

In Figure 2, as in Figure 1, solid bars indicate viscosity and hatched bars % transmission. The mixtures tested (with results in correspondingly numbered bars in Figure 2) were as follows:

1. Surfactant + polymer A in bleach
2. Polymer A in bleach
- 5 3. Surfactant + polymer A in water
4. Polymer A in water
5. Surfactant in bleach
6. Surfactant + polymer B in bleach
7. Polymer B in bleach
- 10 8. Surfactant + polymer B in water
9. Polymer B in water.

The results of Examples 2 and 3 show that cross-linked polymers generally give higher viscosities but lower clarities in hypochlorite than do non-cross-linked polymers. Further work (details not included) has shown that the effect is magnified in the presence of perfume/fragrance.

- 15 Similar experiments using 5% hypochlorite solutions show that cross-linked polymers are less compatible with these systems leading to cloudier solutions which are more unstable.

Based on this and other experimental data, a thickened bleach composition suitable for general domestic use was prepared.

20 Example 4. Thickened bleach composition using polymer A

A thickened 5% hypochlorite formulation was made by mixing the following ingredients:

Component	Use Level (%) (% w/w active matter)
25 Empicol MD (30% active)	2
Empicol ESB3 (27.5% active)	1
Polymer A (31% active)	1.74
30 Sodium hypochlorite (14% active)	5
Fragrance	0.3%
Water	100%

pH was adjusted to 13 with 4% caustic.

The resulting composition had a clear aspect and a viscosity (Brookfield) 3/20 rpm of 275 mPas. and is suitable for use eg as a domestic multi-surface cleaning product.

40 Example 5

Experiments were carried out on compositions comprising polymer A, sodium hypochlorite and various surfactants, and from the information obtained suitable formulations for a hard surface cleaner and a lavatory cleaner with bleach were obtained.

- 45 Formulations containing polymer A were made using the following addition order of ingredients. The polymer was first dispersed in deionised water before caustic solution was added. When fully neutralised to pH13, the relatively soluble surfactants were added with gentle stirring followed by addition of the cosurfactant, fragrance and dye. Lastly, sodium hypochlorite solution was added dropwise and the formulation stirred for a further 10 to 15 minutes before a measurement of initial viscosity was made on a Haake viscometer.

- 50 Results are given in Table 1:

Table 1:

Hypochlorite Formulations containing mixtures of soluble surfactants		
INGREDIENTS	%W/W ACTIVE	
Polymer A	0.5	0.5
Sodium Laurylether Sulphate (Perlankrol ESD)	2.0	1.3
Amine Oxide	0.5	1.3
Sodium Hypochlorite	2.0	2.0
Sodium Hydroxide	0.7	0.7
Viscosity AT 106s ⁻¹	460 mPas	220 mPas

These formulations however are not cost effective and have only moderate cleaning power. By choosing combinations of soluble and insoluble surfactants, cleaning efficiency can be improved and more importantly raw material costs reduced. At a given surfactant level of 3.0%, low viscosity mixtures of ether sulphate (Perlankrol ESD) (SLES) and alkylbenzene sulphonate (Nansa SL30) (LABS) containing 2% w/w bleach are thickened by the addition of 0.5% active polymer A. Formulation viscosity and clarity are varied by altering the relative proportions of ether sulphate and alkyl benzene sulphonate. Results are shown in Figure 3, with solid bars indicating viscosity and hatched bars transmittance. All formulations were thickened with 0.5% polymer A. Viscosity measurements were taken at 25°C. Transmission measurements were taken at 450 nm, path length 1cm. The mixtures tested (with results in correspondingly numbered bars) included surfactant as follows:

1. 3% Perlankrol ESD
2. 2% Perlankrol ESD, 1% Nansa SL30
3. 1.75% Perlankrol ESD, 1.25% Nansa SL30
4. 1.5% Perlankrol ESD, 1.5% Nansa SL30

Variations in the total level of surfactant used, at a constant ratio of SLES to LABS of 4:1 by weight in combination with 0.5% w/w active Polymer A and 2% hypochlorite, provide another means of controlling formulation viscosity and raw material costs. Figure 4 is a plot of viscosity versus total surfactant for this system.

From this work a formulation suitable for use as a hard surface cleaner is obtained:

FORMULATION A: Hard Surface Cleaner	
INGREDIENT	% W/W ACTIVE
Polymer A	0.5%
LABS	0.5%
Sodium Lauryl Ether Sulphate	2.0%
Sodium Hydroxide	0.7%
Fragrance	qs
Dye	qs
Sodium Hypochlorite	2.0%

Formulation A has an initial viscosity of 800 mPas, at a shear rate of 106s⁻¹. The formulation has good long term storage stability and resistance to phase separation over three freeze/thaw cycles. Results of viscosity measurements with time on various samples made without fragrance or dye are shown in Figure 5, providing an indication of stability with time.

Example 6

An assessment of the wetting and cleaning efficiency of several formulations containing Polymer A compared to a control and commercially available products was made as follows.

A model soil comprising of 100g olive oil, 10g instant coffee and 10g of carbon black was applied in thin films to 3 clean, dry ceramic tiles and the soiled tiles conditioned in an incubator for 2 days at 40°C. A 1g aliquot of one of the formulations or a commercial product was pipetted onto the centre of a tile and after 2 minutes, an estimate of the area over which the liquid had spread was made. The wetted area was then rubbed with a small brush with light pressure. The amount of soil removed was assessed visually by estimating the area of tile exposed by rubbing.

The cleaning efficiency of Formulation A was assessed by this method. Results are given in Table 2. A non-optimised formulation comprising ether sulphate and amine oxide cleaner with 0.5% polymer was used as a control, and results were also obtained for a commercially available multi-surface cleaner. Results are given below.

Table 2 -

Cleaning efficiency of Formulation A compared to a commercial brand.		
FORMULATION	SPREADING PROPERTIES	CLEANING EFFICIENCY
Formulation A	Good	Good
Commercially available multi-surface cleaner	Very Good	Good
Control	Poor	Poor

Example 7

With the benefit of this information, a cost effective low viscosity lavatory cleaner formulation with lower total surfactant levels can be obtained, as specified in formulation B below.

FORMULATION B: Lavatory Cleaner with Bleach	
INGREDIENT	%W/W ACTIVE
Polymer A	0.5%
LABS	0.4%
Sodium Lauryl Ether Sulphate	1.7%
Sodium Hydroxide	0.7%
Fragrance	qs
Dye	qs
Sodium Hypochlorite	2.0%

Formulation B has an initial viscosity of 300 mPas at a shear rate of 106s⁻¹

Example 8

At higher levels of bleach (greater than 3%), the dissolved electrolyte levels are sufficient to effect surfactant thickening. However, there are still limits to the viscosities that can be achieved often due to the fact that the level of electrolyte is fixed. In this instance, low levels of polymer A can be used to increase viscosity or to lower the amount of surfactant required to achieve target viscosity.

A thickened formulation containing 5.0% active sodium hypochlorite can be made as follows:

FORMULATION C: Premium thickened Bleach Product	
INGREDIENT	%W/W ACTIVE
Polymer A	1.0%
Sodium Lauryl ether Sulphate	3.0%
Sodium Hydroxide	0.7%
Fragrance	qs
Dye	qs
Sodium Hypochlorite	5.0%
Viscosity	130 mPas at shear rate of 106s ⁻¹

At lower levels of bleach, for example 4.0% sodium hypochlorite, the viscosity of the formulation depends to a large extent on the dissolved electrolyte and is less dependent on the amount of polymer A.

Significant increases in viscosity are still observed however when polymer A is incorporated into a formulation at 1% w/w active polymer. Results are given in Table 4 below.

Table 4 -

Formulation containing 4% Sodium Hypochlorite		
INGREDIENT	%W/W ACTIVE	
Polymer A		1.0
Sodium Lauryl Ether Sulphate	3.0	3.0
Sodium Hypochlorite	4.0	4.0
Viscosity	Phase separation occurs	35 mPas

Claims

1. A bleach composition, comprising an active halogen or a peroxy bleach material; surfactant; and polymeric thickener comprising charged, hydrophilic monomer and uncharged, hydrophobic monomer.
2. A composition according to claim 1, wherein the charged, hydrophilic monomer is selected from group: acrylic acid and substituted acrylic acids, eg. methacrylic acid, maleic acid and half-esters thereof, crotonic and itaconic acids and other alkene carboxylic acids and their derivatives, carboxylated styrene, sulfonated styrene, ethylene sulphonic acid, and certain nitrogen-based monomers eg acrylamide, vinyl pyrrolidone, and mixtures of such hydrophilic monomers.
3. A composition according to claim 1 or 2, wherein the uncharged hydrophobic monomer is selected from the group: styrene and substituted styrenes eg. alpha-methyl styrene, alpha-olefins, eg. C₁₂-alpha-olefin, vinyl ethers, eg. butyl vinyl ether; allyl ethers, eg. butyl allyl ether; unsaturated hydrocarbons, eg ethylene, propylene, cyclohexene and dienes, eg. 1,6 hexadiene, divinyl benzene, cyclohexadiene.
4. A composition according to claim 1, 2 or 3, wherein the polymeric thickener comprises a copolymer of methacrylic acid and styrene, preferably having proportions (wt %) of methacrylic acid and styrene ranging from 80:20 to 20:80.
5. A composition according to any one of the preceding claims, wherein the polymeric thickener is substan-

tially non cross-linked.

6. A composition according to any one of the preceding claims, wherein the polymeric thickener has a molecular weight of about 100,000.
- 5 7. A composition according to claim 6, wherein the polymeric thickener comprises 54 wt% methacrylic acid and 46% styrene, with a molecular weight of about 100,000 and substantially no cross-linking.
8. A composition according to any one of the preceding claims, wherein the polymeric thickener is present in an amount from 0.1 to 7.5% by wt as active material, preferably 0.5 to 3% by wt as active material.
- 10 9. A composition according to any one of the preceding claims, wherein the bleach material comprises one or more halogen compounds, including alkali metal and alkaline earth salts of hypohalite, haloamines, haloimines, haloimides and haloamides.
- 15 10. A composition according to claim 9, wherein the bleach material comprises hypochlorite or compounds producing hypochlorite in aqueous solution.
11. A composition according to claim 10, wherein the bleach material comprises sodium hypochlorite, preferably in an amount ranging from 0.2 to 15% by weight, more preferably 0.2 to 10% by weight.
- 20 12. A composition according to any one of the preceding claims, wherein the surfactant comprises one or more surfactants selected from the following: alkyl ether sulphates, eg lauryl ether sulphate, alcohol sulphates, eg lauryl alcohol sulphate, tallow alcohol sulphates, alkyl benzene sulphonates, paraffin sulphonates, alkyl phenol ether sulphates, alcohol ethoxylates, nonylphenol ethoxylates, sodium carboxylates (soaps) (salts of fatty acids), alkyl ether carboxylates, alkyl polyglucosides, EP/PO block copolymers, alkyl diphenyloxide sulphonates, fatty acid amides, acyl sarcosinates, alkyl laurides, sulphosuccinates, alpha-olefin sulphonates, phosphate ester (alkyl and/or aryl), ethoxylated fatty acids, triethanolamine lauryl sulphate, triethanolamine alkyl benzene sulphonate, sodium lauryl sulphate, sodium alpha olefin sulphonate.
- 25 13. A composition according to any one of the preceding claims, wherein surfactant is present in an amount in the range 0.5 to 5% by wt active matter, preferably about 2% to 3% by wt active matter.
14. A composition according to any one of the preceding claims, comprising over about 3% by weight active hypochlorite, wherein the surfactant has a cloud point below about 0°C.
- 35 15. A composition according to claim 14, wherein the surfactant comprises one or more of the following: sodium lauryl ether sulphate, triethanolamine lauryl sulphate and triethanolamine alkyl benzene sulphonate.
16. A composition according to any one of claims 1 to 13, comprising less than about 3% by weight active hypochlorite, wherein the surfactant comprises a mixture of surfactant having a cloud point below about 0°C and surfactant having a cloud point above about 0°C.
- 40 17. A composition according to claim 16, wherein the surfactant having a cloud point below about 0°C comprises one or more of the following: sodium lauryl ether sulphate, triethanolamine lauryl sulphate and triethanolamine alkyl benzene sulphonate, and the surfactant having a cloud point above about 0°C comprises one or more of the following: sodium alkyl benzene sulphonate, sodium lauryl sulphate and sodium alpha olefin sulphonate.
- 45 18. A composition, according to any one of the preceding claims, further comprising electrolyte.
19. A composition according to any one of the preceding claims, further comprising buffer.
- 50 20. A composition according to any one of the preceding claims, having a pH between 11 and 14, preferably about 13.
21. A composition according to any one of the preceding claims, further comprising one or more of the following: fragrance, colouring agents, whiteners, solvents and builders.
- 55 22. A composition according to any one of the preceding claims, wherein the bleach comprises hypochlorite and the polymeric thickener comprises 54% methacrylic acid and 46% styrene with a molecular weight

of about 100,000, being substantially non-cross-linked.

23. A composition according to claim 22, wherein the amount of hypochlorite is greater than about 3% by wt active and the surfactant comprises sodium lauryl ether sulphate.
- 5 24. A composition according to claim 22, wherein the amount of hypochlorite is less than about 3% by wt active, and the surfactant comprises a mixture of sodium alkyl benzene sulphonate and sodium lauryl ether sulphonate.
- 10 25. A composition according to any one of the preceding claims in the form of a hard surface cleaner, multi-surface cleaner, toilet cleaner or drain cleaners.

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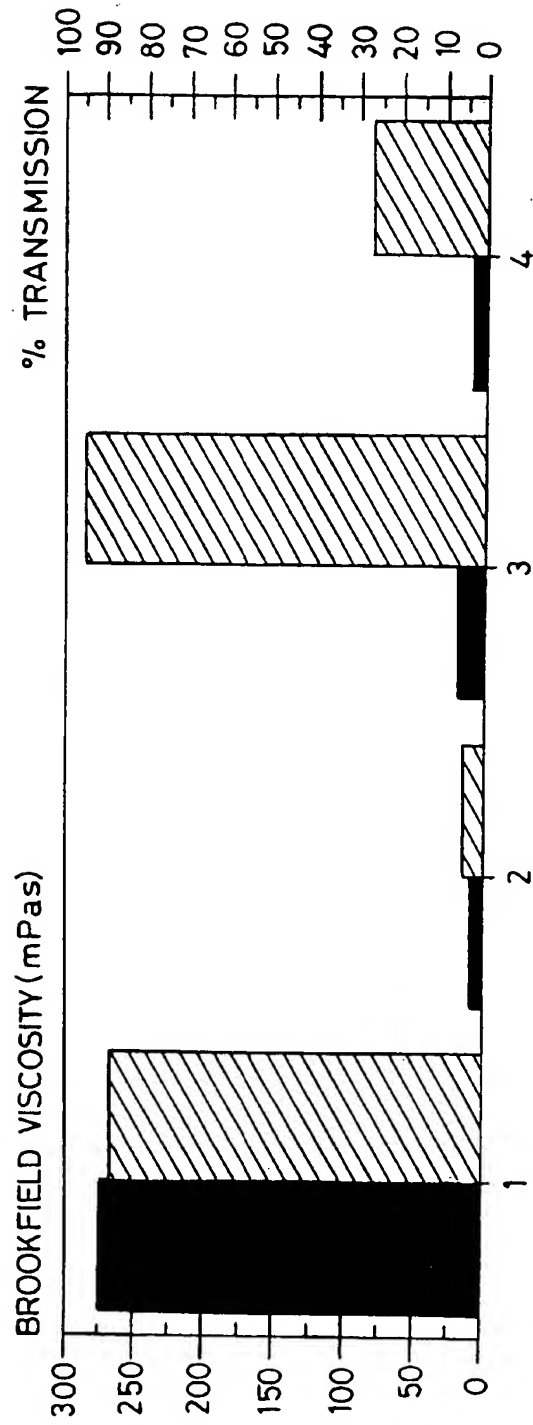


Fig. 1

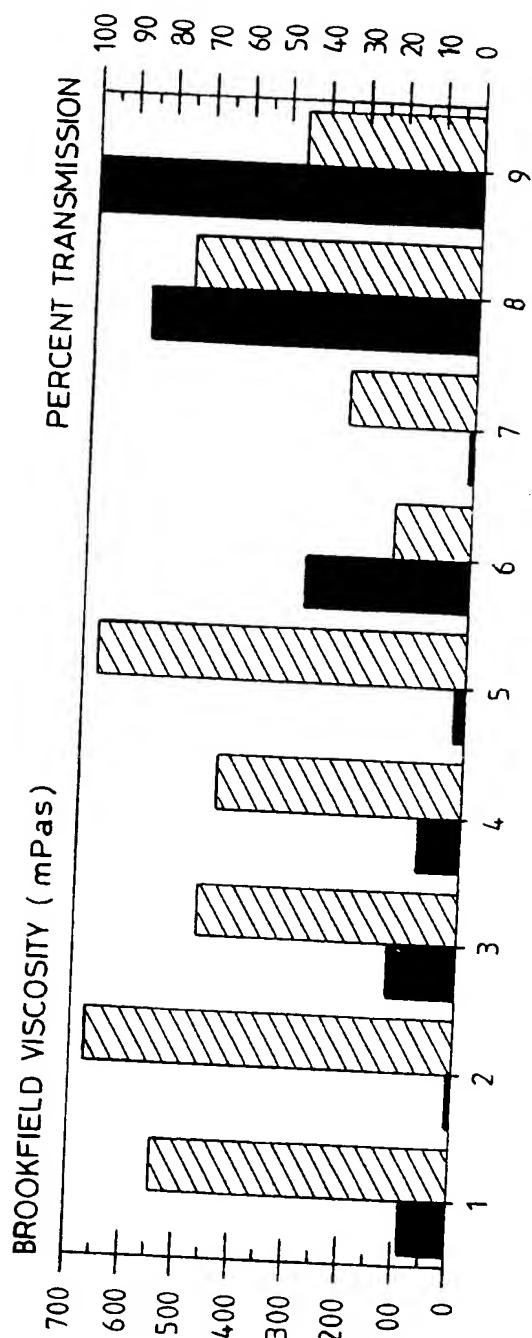


Fig. 2

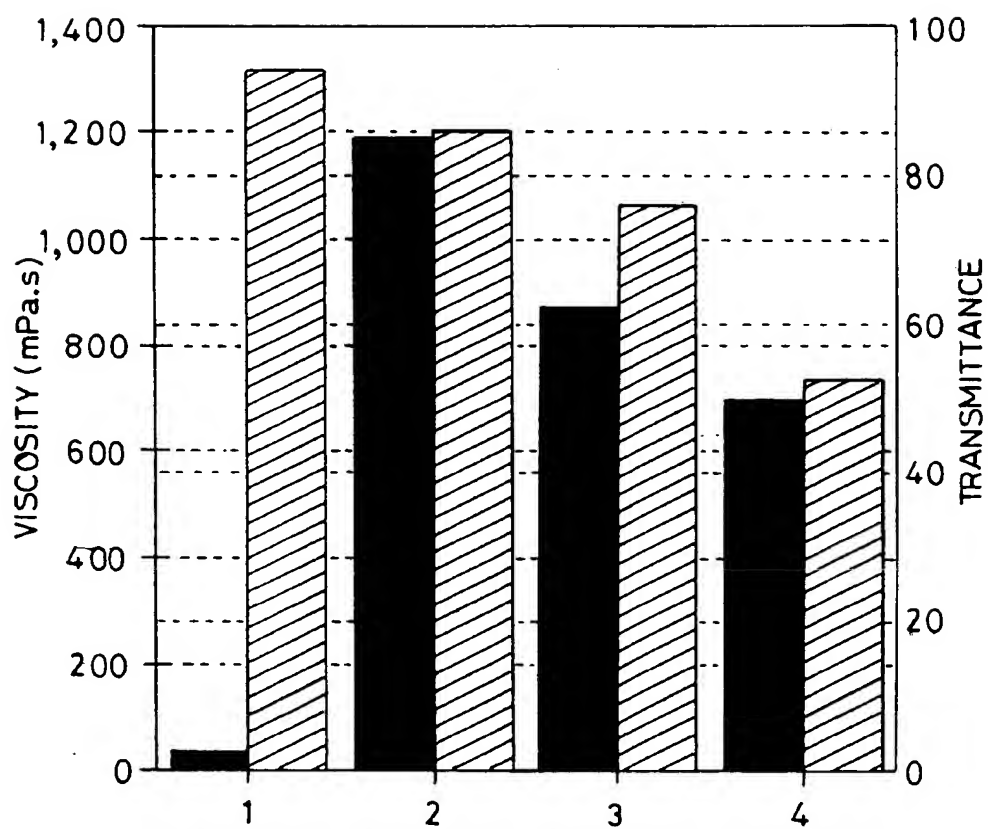


Fig. 3

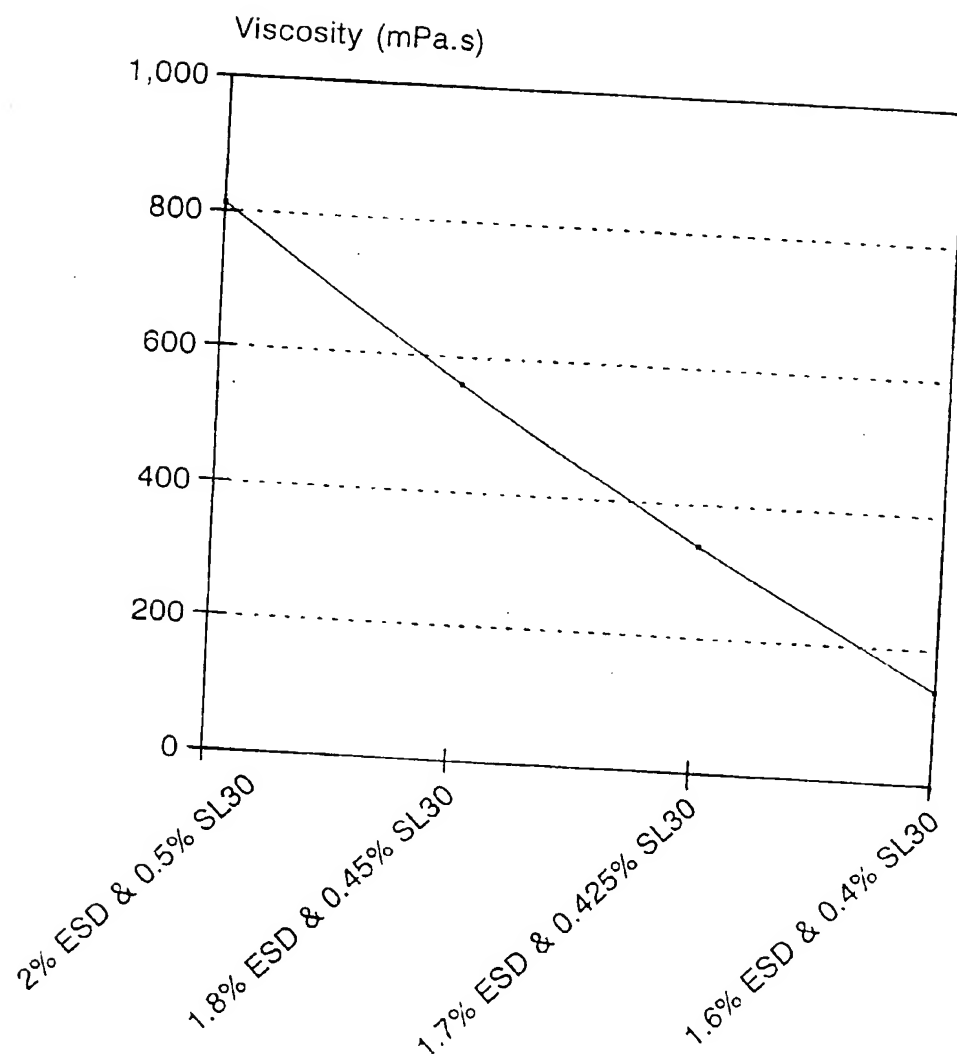


Fig. 4

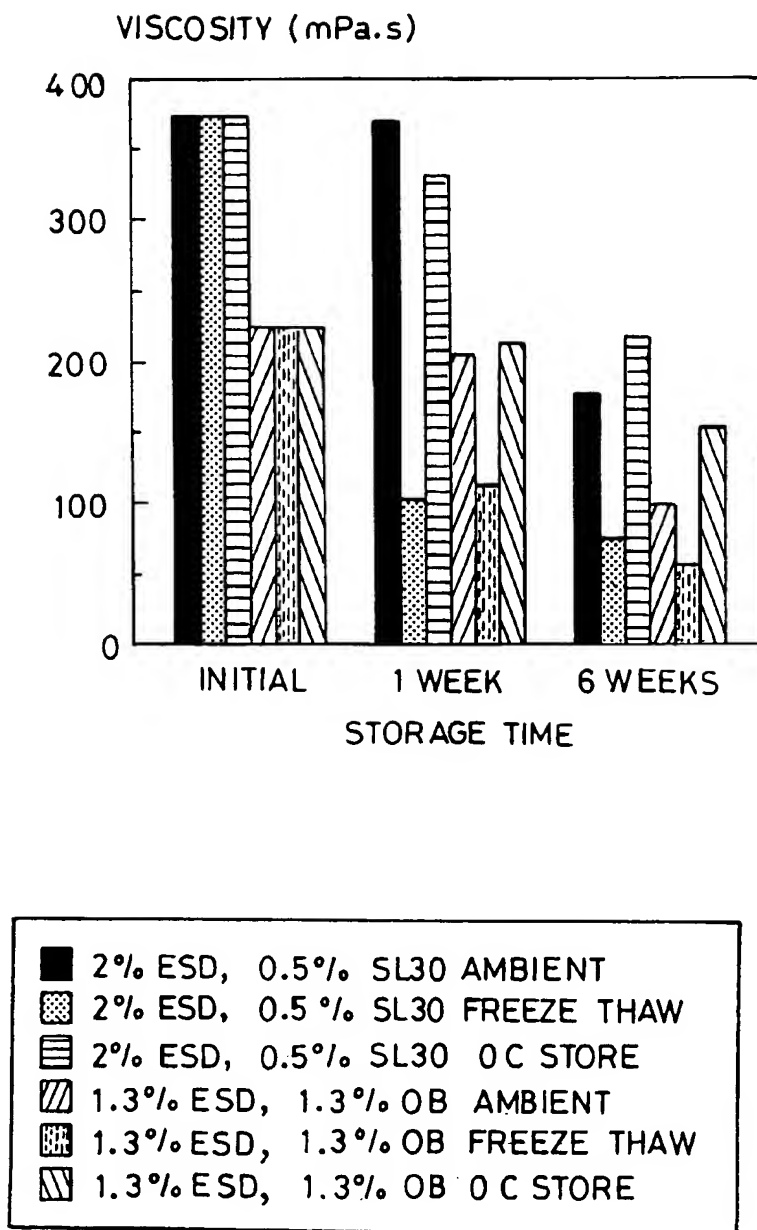


Fig. 5

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(54) Bleach compositions

(57) A bleach composition comprises an active halogen or a peroxy bleach material, preferably hypochlorite; surfactant; and polymeric thickener comprising charged, hydrophilic monomer and uncharged hydrophobic monomer. The polymeric thickener preferably comprises a copolymer of methacrylic acid and styrene having proportions (wt%) of methacrylic acid and styrene ranging from 80:20 to 20:80, and preferably comprises 54 wt% methacrylic acid and 46% styrene, with a molecular weight of about 100,000 and substantially no cross-linking. The polymeric thickener acts to enhance thickening and enables use of a wider range of surfactants than hitherto possible.

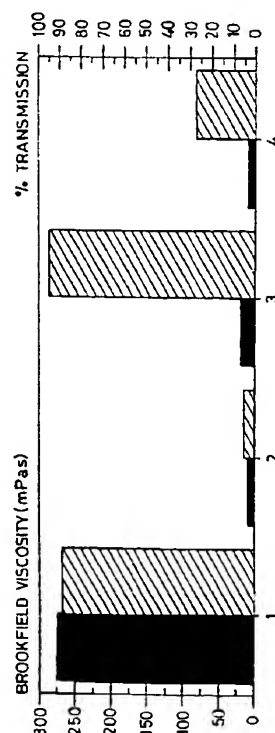


Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	EP-A-0 256 638 (CLOROX CO) *abstract* * page 9, line 32-35 * * page 12, line 20-35 * * claims 1-5 *	1-3,6, 8-11, 18-21,25	C11D3/395 C11D3/37 C11D3/39
D,X	EP-A-0 329 419 (UNILEVER PLC ;UNILEVER NV (NL)) * page 3, last paragraph * * page 4, last paragraph * * claims *	1-4,6, 8-12, 19-21	
Y	EP-A-0 385 522 (UNILEVER NV ;UNILEVER PLC (GB)) * page 6, line 48-55 * * claims *	1-4, 8-13, 18-21	
Y	EP-A-0 244 006 (UNILEVER NV ;UNILEVER PLC (GB)) * page 3, line 21-29 * * page 4, line 35 *	1-4, 8-13, 18-21	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
A	EP-A-0 346 995 (UNILEVER NV ;UNILEVER PLC (GB)) * page 6, line 51-52 *		
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 22 February 1996	Examiner Pelli Wablat, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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